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<p>(21) International Application Number: PCT/US90/00485 (22) International Filing Date: 24 January 1990 (24.01.90) (30) Priority data: 302,845 25 January 1989 (25.01.89) US (71) Applicant: RAYCHEM CORPORATION [US/US]; 300 Constitution Drive, Menlo Park, CA 94025 (US). (72) Inventors: LUNK, Hans, E. ; 1145 Monte Rosa Drive, Menlo Park, CA 94025 (US). TONDRE, Stephen, L. ; 33455 Caliban Drive, Fremont, CA 94555 (US). (74) Agent: RICE, Edith, A. ; Raychem Corporation, 300 Con- stitution Drive, Menlo Park, CA 94025 (US).</p>		<p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: FLUOROPOLYMER COMPOSITIONS

(57) Abstract

A fluoropolymer composition which can be marked by a laser, e.g. a Nd:YAG laser, contains about 2 to about 7 % of an energy absorber and about 1 to about 15 % of a mark enhancing organic compound having a decomposition temperature above the processing temperature of the fluoropolymer, all percentages being by weight based on the weight of the fluoropolymer. The composition undergoes a visible change, preferably irreversible, when exposed to the laser. The fluoropolymer composition can comprise a surface layer, such as a coating, on an article, such as an electrical conductor. The fluoropolymer composition can itself be formed into a shaped article, in particular a heat recoverable article.

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FLUOROPOLYMER COMPOSITIONS

This invention relates to a laser markable fluoropolymer composition, an article, such as an electrical conductor coated therewith, a shaped article, in particular a heat recoverable article, formed from said composition, a method of rendering a fluoropolymer markable by a laser and a method of marking a fluoropolymer surface using a laser.

Fluoropolymers are known to be difficult to mark by conventional printing methods. It is at times desirable to mark a fluoropolymer surface, e.g. a fluoropolymer wire coating or cable jacket, marker sleeves, or the like.

The use of lasers to mark polymeric articles is disclosed in the literature. For example, U.S. Patent No. 4,307,047 to Edinger et al, discloses marking typewriter keys molded from a plastic material, such as ABS, containing a filler capable of undergoing a color change, for example iron oxide-hydroxide. In U.S. Patent No. 4,118,229, Stromberger-D'Alton-Rauch, et al disclose using a laser beam to record visible data on a polymeric layer containing acetyl acetate. In U.S. Patent No. 4,443,571, Needham et al disclose using a laser to mark a polyarylene sulfide composition containing an additive system, for example, nickel-antimony-titanium, or monoazo-nickel complex. The incorporation of various fillers such as fiberglass, talc, titanium dioxide, silica or calcium sulfate is mentioned. U.S. Patent No. 4,654,290 to Spanjer discloses laser marking of a composition comprising a resin, such as an epoxy, silicone or polyimide, titanium dioxide and optionally an inorganic additive such as chromium oxide or carbon black. The composition may also contain a filler such as aluminum

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oxide and silicon oxide. Australian Patent Application 52821/86 to Guggen et al discloses laser marking various polymers containing a radiation sensitive additive that effects a change in color. The additive can be for example, an inorganic or organic pigment or polymer soluble dye.

None of these references mentions a fluoropolymer and thus none suggests a fluoropolymer composition which is laser markable, nor that a fluoropolymer is capable of being rendered laser markable.

One aspect of this invention provides a laser markable composition comprising a fluoropolymer having a processing temperature above about 250°C, about 2 to about 7% by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from a laser and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark enhancing organic compound having a decomposition temperature above the processing temperature of the fluoropolymer, the composition being capable of undergoing a visible color change when exposed to a laser.

A further aspect of this invention provides an article coated on the surface thereof with a fluoropolymer composition comprising a fluoropolymer having a processing temperature above about 250°C, about 2 to about 7% by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from a laser, and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark enhancing organic compound having a decomposition temperature above the processing temperature of the

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fluoropolymer, said composition being capable of undergoing a visible change when exposed to a laser.

An additional aspect of this invention provides a heat recoverable article formed from a fluoropolymer composition comprising a fluoropolymer having a processing temperature above about 250°C, about 2 to about 7% by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from a laser, and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark enhancing organic compound having a decomposition temperature above the processing temperature of the fluoropolymer.

Another aspect of this invention provides a method of rendering a fluoropolymer markable by a laser which comprises admixing with the fluoropolymer about 2 to about 7 % by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from the laser and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark enhancing organic compound having a decomposition temperature above the processing temperature of the fluoropolymer.

Yet another aspect of this invention provides a method of marking a surface comprising a fluoropolymer composition which comprises incorporating in the fluoropolymer composition, about 2 to about 7% by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from a laser, and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark

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enhancing organic compound having a decomposition temperature above the processing temperature of the fluoropolymer and exposing the surface of the composition to a laser.

Fluoropolymers suitable for use in this invention include thermoplastic and elastomeric fluoropolymers, for example, tetrafluoroethylene homo- and copolymers, such as polytetrafluoroethylene, ethylene-tetrafluoroethylene copolymers tetrafluoroethylene-propylene copolymers; vinylidene fluoride homo- and copolymers, such as polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymers, vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene terpolymers,; perfluoroalkoxy polymers; fluorinated ethylene-propylene copolymers; and the like. Preferred fluoropolymers are ethylene-tetrafluoroethylene copolymers (ETFE).

The composition of this invention comprises about 2 to about 7% by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from the laser employed. Preferably the composition comprises about 2 to about 5% of the energy absorber and most preferably about 2 to about 4%, all percentages being by weight, based on the weight of the fluoropolymer.

The energy absorber employed depends, in part, on the laser selected. For example, with a neodymium yttrium-arsenic-garnet (Nd:YAG) laser, titanium dioxide is a preferred energy absorber.

It has been found that addition of the energy absorber alone does not result in acceptable marking of the fluoropo-

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lymer surface when exposed to the laser. The composition of this invention further comprises a mark enhancing organic compound having a decomposition temperature higher than the melt processing temperature of the particular fluoropolymer. (Fluoropolymers, in general, have relatively high processing temperatures, about 220 to about 400°C. Commercially available ethylene-tetrafluoroethylene copolymers, preferred in the practice of this invention, have melting points of about 220°C to about 280°C.) The organic compound alone does not impart laser markability to the fluoropolymer. However, a fluoropolymer composition containing the energy absorber and the organic compound are readily markable by a laser. Suitable organic compounds can readily be determined by one skilled in the art. One quick method for identifying mark enhancing compounds is to select compounds having a decomposition temperature above the processing temperature of the fluoropolymer and then heating the compound to a temperature of about 400°C to see if it undergoes a visible color change. The compositions of this invention are typically light in color and the resulting laser mark is dark. Compositions comprising only one of the energy absorber or organic compound or inadequate amounts of either compounds, unlike the compositions of this invention, are not readily markable by a laser. If the energy output of the laser is adjusted to provide sufficient energy to mark such a composition, damage to the fluoropolymer composition may result. Compositions of this invention are markable at relatively low energy levels and the fluoropolymer composition suffers no detrimental effects.

Preferred organic compounds are sulfur-containing compounds, such as distearyl thiodipropionate, dilauryl thio-

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dipropionate or oligomers thereof, 4,4'-thiobis(6-t-butyl-m-cresol), or the like, hydroxy-containing compounds, such as tetrakis (methylene 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane, 2,2'-oxamidobis(ethyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, resorcinol monoacetate, or the like, nitrogen-containing compounds, such as triallyl isocyanurate, triallyl cyanurate, bis-melaminium pentate, acetylene diurene, L- -alanine, melamine, acetanilide, guanine, dibenzylamine, dibenzylidiphenylamine, 4,4'-bis(dimethylamino)-benzophenone, or the like, phosphorus-containing compounds, such as tetrakis (2,4-di-t-butylphenyl)-4,4'biphenylene diphosphonate, tris (2,4-di-t-butylphenyl) phosphite, bis (2,4-di-t-butyl) pentaerythritol diphosphite, distearyl pentaerythritol diphosphate, triphenyl phosphate, triphenyl phosphine oxide, or the like, carbonyl-containing compounds, such as magnesium stearate, diphenyl acetaldehyde, ethyl dimalonate, or the like.

The composition of this invention comprises about 1 to about 15% by weight, based on the weight of the fluoropolymer, of the organic compound. Preferably the composition comprises about 2 to about 10% of the organic compound and most preferably about 2 to about 7%, all percentages being by weight, based on the weight of the fluoropolymer.

Various additives can be added to the polymeric composition. Such additives include for example, antioxidants such as alkylated phenols, e.g. those commercially available as Goodrite 3125, Irganox 1010, Irganox 1035, Irganox 1076, Irganox 1093, Vulkanox BKF, organic phosphite or phosphates,

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e.g. dilauryl phosphite, Mark 1178, alkylidene polyphenols, e.g. Ethanox 330, thio-bis alkylated phenol, e.g. Santonox R, dilauryl thio-dipropionate, e.g. Carstab DLTD, dimyristyl thiodipropionate, e.g. Carstab DMTDP, distearyl thiodipropionate, e.g. Cyanox STDP, amines, e.g. Wingstay 29 etc.; UV stabilizers such as [2,2'-thio-bis(4-t-octyl-phenolato)] n-butylamine nickel, Cyasorb UV 1084, 3,5-ditertiarybutyl-phydroxybenzoic acid, UV Chek AM-240; flame retardants such as decabromodiphenyl ether, perchloropentacyclodecane, 1,2-bis(tetrabromophthalimido) ethylene; pigments such as titanium dioxide, antimony trioxide, zinc oxide, iron oxide, etc., and the like. Mixtures of such additives can be used. Certain of these additives can also function as the organic compound if present in the stipulated amounts.

The composition of this invention can be prepared by mixing the fluoropolymer, energy absorbing compound and organic compound in an internal mixer such as a Banbury or Brabender, a twin screw extruder such as a Brabender or ZSK, or the like, at a temperature above the melting temperature of the fluoropolymer (or above the processing temperature if the fluoropolymer is elastomeric).

The composition of this invention can be crosslinked, if desired. Crosslinking can be achieved for example by use of a suitable cross-linking agent, such as a peroxide or amine, or by irradiation.

In a preferred embodiment, the composition is cross-linked by irradiation. The dosage employed in the

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irradiation step is generally below about 50 Mrads to ensure that the polymer is not degraded by excessive irradiation. The dosage preferably employed depends upon the extent of cross-linking desired, balanced against the tendency of the polymer to be degraded by high doses of irradiation. Suitable dosages are generally in the range 2 to 40 Mrads, for example 2 to 30 Mrads, preferably 3 to 20 Mrads, especially 4 to 25 or 4 to 20 Mrads, particularly 4 to 15 Mrads. The ionizing radiation can for example be in the form of accelerated electrons or gamma rays. Irradiation is generally carried out at about room temperature, but higher temperatures can also be used.

Prior to irradiation it is preferred to incorporate a cross-linking agent into the composition. Preferred radiation cross-linking agents contain carbon-carbon unsaturated groups. In many cases the cross-linking agent contains at least two ethylenic double bonds, which may be present, for example, in allyl, methallyl, propargyl, or vinyl groups. Preferred cross-linking agent contain at least two allyl groups, especially three or four allyl groups. Particularly preferred cross-linking agents are triallyl cyanurate (TAC) and triallyl isocyanurate (TAIC); other specific cross-linking agents include triallyl trimellitate, triallyl trimesate, tetraallyl pyromellitate, the diallyl ester of 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl) indan. Other cross-linking agents which are known for incorporation into fluorocarbon polymers prior to shaping, for example those disclosed in U.S. Patents Nos. 3,763,222, 3,840,619, 3,894,118, 3,911,192, 3,970,770, 3,985,716, 3,995,091, 4,031,167, 4,155,823 and 4,353,961.

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Mixtures of cross-linking agents can be used. Certain of these cross-linking agents can be used as the organic compound if present in appropriate amounts.

The compositions can be formed into shaped articles, coatings, or the like, by melt processing, lamination, extrusion or other suitable techniques. A preferred use of the composition of this invention is as an insulation for an elongate electrical conductor, such as a wire or cable. The composition is preferably coated onto the conductor by extrusion, but can be applied by any other method such as tape wrapping or the like.

Another preferred use of the composition of this invention is in the preparation of heat recoverable articles, particularly articles for use as marker sleeves for wire and cable. A heat recoverable article is one whose dimensional configuration may be made to change when subjected to an appropriate treatment.

Usually these articles recover, on heating, towards an original shape from which they have previously been deformed but the term "heat-recoverable," as used herein, also includes an article which, on heating, adopts a new configuration, even if it has not been previously deformed.

In their most common form, heat-recoverable articles comprise a heat-shrinkable sleeve made from a polymeric material exhibiting the property of elastic or plastic memory as described, for example, in U.S. Patents Nos. 2,027,962, 3,086,242 and 3,597,372. As is made clear in, for example, U.S. Patent No. 2,027,962, the original dimen-

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sionally heat-stable form may be a transient form in a continuous process in which, for example, an extruded tube is expanded, while hot, to a dimensionally heat-unstable form but, in other applications, a preformed dimensionally heat-stable article is deformed to a dimensionally heat-unstable form in a separate stage.

In the production of heat-recoverable articles, the polymeric material may be cross-linked (as discussed above) at any stage in the production of the article that will enhance the desired dimensional recoverability. One manner of producing a heat-recoverable article comprises shaping the polymeric article into the desired heat-unstable form, subsequently cross-linking the polymeric material, heating the article to a temperature above the crystalline melting point of the polymer, deforming the article and cooling the article whilst in the deformed state so that the deformed state of the article is retained. In use, since the deformed state of the article is heat-unstable, application of heat will cause the article to assume its original heat-stable shape.

The following examples illustrate the preparation of laser markable compositions in accordance with this invention and marking the compositions with a laser.

Example 1

Sample Preparation

Compositions were prepared by blending an ethylene-tetrafluoroethylene copolymer, ETFE, (Tefzel HT-2055 commer-

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cially available from du Pont), titanium dioxide, and an organic compound in amounts specified in Table I in a Brabender twin screw mixer at 290°C (all zones of the mixer) and at 20 rpm. The organic compounds are designated as follows:

- Irg 1010 = Tetrakis(methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane
(commercially available as Irganox 1010 from Ciba-Geigy)
- DS-TDP = Distearyl thiodipropionate (obtained from Evans Chemetics)
- Irgaf 168 = Tris(2,4-di-t-butylphenyl)-4,4'-phosphite
(commercially available as Irgafos 168 from Ciba-Geigy)
- TAIC = triallylisocyanurate.

Evaluation

Slabs 0.025"x6"x6" were pressed of each test sample. Each slab was exposed to a Nd:YAG laser (Blazer 2000 from Quantrad) set at 0.5-1.2 watts, 22.5-28.5 amps at 1 kHz. The laser was set in the dot matrix mode. The results are shown in Table I.

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Table I

<u>Sample No.</u>	<u>ETFE</u>	<u>TiO₂</u>	<u>Irg 1010</u>	<u>DSTDP</u>	<u>Irgaf 168</u>	<u>TAIC</u>	<u>MARK'</u>
1	100%	0	-	-	-	-	NM
2	98%	0	-	-	2%	-	NM
3	99%	1%	-	-	-	-	VL
4	97%	1%	2%	-	-	-	L
5	97%	1%	-	2	-	-	L
6	97%	1%	-	-	2	-	L
7	97%	1%	-	-	-	2	L
8	92%	1%	-	-	-	7	VL
9	98%	2%	-	-	-	-	VL
10	96%	2%	-	-	2	-	M
11	96%	2%	-	-	-	2	G
12	97%	3%	-	-	-	-	L
13	95%	3%	2	-	-	-	VG
14	95%	3%	-	2	-	-	E
15	95%	3%	-	-	2	-	G
16	95%	3%	-	-	-	2	E
17	90%	3%	-	-	-	7	VG
18	95%	5%	-	-	-	-	L
19	93%	5%	-	-	-	2	G
20	88%	5%	-	-	-	7	L

- (1) NM = no mark
 L = light mark
 VL = very light mark
 G = good mark
 VG = very good mark
 E = excellent mark

Example 2Sample Preparation

Compositions were prepared by blending a fluorinated ethylene-propylene copolymer (FEP commercially available from du Pont), titanium dioxide, an organic compound and

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various additives as set forth in Table II in a Brabender internal mixer having a 60 cc mixing bowl at a temperature of 335°C and run at 50 rpm.

Evaluation

Slabs .025"x6"x6" of each sample were pressed at 335°C. Each slab was exposed to a Nd:YAG laser (Blazer 2000) set at 0.72 - 1.5 watts, 25-33 amps. 1 kHz in a dot matrix mode. The results are reported in Table II.

Table II

<u>Sample No.</u>	<u>FEP</u>	<u>TiO₂</u>	<u>Irg 1010</u>	<u>Mark²</u>
1	100%	--	--	NM
2	97%	3%	--	NM
3	95%	3%	2%	L

(2) NM = no mark

L = light mark

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What is claimed is:

1. A laser markable composition comprising a fluoropolymer having a processing temperature above about 250°C, about 2 to about 7% by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from a laser and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark enhancing organic compound having a decomposition temperature above the processing temperature of the fluoropolymer, the composition being capable of undergoing a visible color change when exposed to a laser.
2. A composition in accordance with claim 1, wherein the fluoropolymer is selected from the group consisting of tetrafluoroethylene homo- and copolymers, vinylidene fluoride homo- and copolymers, perfluoroalkoxy polymers and fluorinated ethylene-propylene copolymers.
3. A composition in accordance with claim 2, wherein the fluoropolymer is an ethylene-tetrafluoroethylene copolymer.
4. A composition in accordance with claim 1, wherein said energy absorbing compound is titanium dioxide.
5. A composition in accordance with claim 1 or claim 4, wherein the organic compound is selected from the group consisting of sulfur-containing compounds, hydroxy-containing compounds, nitrogen-containing compounds, phosphorus containing compounds and carbonyl-containing compounds.
6. A composition in accordance with claim 5, wherein the organic compound is selected from the group consisting of

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tetrakis (methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane, distearyl thiodipropionate, tris (2,4-di-t-butylphenyl)-4,4'-phosphite and triallylisocyanurate.

7. An article coated on the surface thereof with a fluoropolymer composition comprising a fluoropolymer having a processing temperature above about 250°C, about 2 to about 7% by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from a laser, and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark enhancing organic compound having a decomposition temperature above the processing temperature of the fluoropolymer, said composition being capable of undergoing a visible change when exposed to a laser.

8. An article in accordance with claim 7 which is an electrical conductor.

9. An article in accordance with claim 7 which is a wire or cable.

10. An article in accordance with claim 7, wherein the fluoropolymer is selected from the group consisting of tetrafluoroethylene homo- and copolymers, vinylidene fluoride homo- and copolymers, perfluoroalkoxy polymers and fluorinated ethylene-propylene copolymers.

11. An article in accordance with claim 10, wherein the fluoropolymer is an ethylene-tetrafluoroethylene copolymer.

12. An article in accordance with claim 7, wherein said energy absorbing compound is titanium dioxide.

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13. An article in accordance with claim 7 or claim 12, wherein the organic compound is selected from the group consisting of sulfur-containing compounds, hydroxy-containing compounds, nitrogen-containing compounds, phosphorus containing compounds and carbonyl-containing compounds.

14. An article in accordance with claim 13, wherein the organic compound is selected from the group consisting of tetrakis (methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane, distearyl thiodipropionate, tris (2,4-di-t-butylphenyl)-4,4'-phosphite and triallylisocyanurate.

15. A heat recoverable article formed from a fluoropolymer composition comprising a fluoropolymer having a processing temperature above about 250°C, about 2 to about 7% by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from a laser, and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark enhancing organic compound having a decomposition temperature above the processing temperature of the fluoropolymer, said composition being capable of undergoing a visible change when exposed to a laser.

16. A heat-recoverable article in accordance with claim 15 which is a tubular article.

17. A heat-recoverable article in accordance with claim 16 which is a marker sleeve.

18. An article in accordance with claim 15, wherein the fluoropolymer is selected from the group consisting of

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tetrafluoroethylene homo- and copolymers, vinylidene fluoride homo- and copolymers, perfluoroalkoxy polymers and fluorinated ethylene-propylene copolymers.

19. A composition in accordance with claim 18, wherein the fluoropolymer is an ethylene-tetrafluoroethylene copolymer.

20. A composition in accordance with claim 15, wherein said energy absorbing compound is titanium dioxide.

21. A composition in accordance with claim 15 or claim 20, wherein the organic compound is selected from the group consisting of sulfur-containing compounds, hydroxy-containing compounds, nitrogen-containing compounds, phosphorus containing compounds and carbonyl-containing compounds.

22. A composition in accordance with claim 21, wherein the organic compound is selected from the group consisting of tetrakis (methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane, distearyl thiodipropionate, tris (2,4-di-t-butylphenyl)-4,4'-phosphite and triallyliscyanurate.

23. A method of rendering a fluoropolymer markable by a laser which comprises admixing with the fluoropolymer about 2 to about 7 % by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from the laser and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark enhancing organic compound having a decomposition temperature above the processing temperature of the fluoropolymer.

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24. A method in accordance with claim 23, wherein the fluoropolymer is selected from the group consisting of tetrafluoroethylene homo- and copolymers, vinylidene fluoride homo- and copolymers, perfluoroalkoxy polymers and fluorinated ethylene-propylene copolymers.

25. A method in accordance with claim 24, wherein the fluoropolymer is an ethylene-tetrafluoroethylene copolymer.

26. A method in accordance with claim 23, wherein said energy absorbing compound is titanium dioxide.

27. A method in accordance with claim 23 or claim 26, wherein the organic compound is selected from the group consisting of sulfur-containing compounds, hydroxy-containing compounds, nitrogen-containing compounds, phosphorus containing compounds and carbonyl-containing compounds.

28. A method in accordance with claim 27, wherein the organic compound is selected from the group consisting of tetrakis (methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane, distearyl thiodipropionate, tris (2,4-di-t-butylphenyl)-4,4'-phosphite and triallyliscyanurate.

29. A method of marking a surface comprising a fluoropolymer composition which comprises incorporating in the fluoropolymer composition, about 2 to about 7% by weight, based on the weight of the fluoropolymer, of a compound capable of absorbing energy from a laser, and about 1 to about 15% by weight, based on the weight of the fluoropolymer, of a mark enhancing organic compound having a decomposition tem-

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perature above the processing temperature of the fluoropolymer and exposing the surface of the composition to a laser.

30. A method in accordance with claim 29 wherein the surface is exposed to a Nd:YAG laser.

31. A method in accordance with claim 29, wherein the fluoropolymer is selected from the group consisting of tetrafluoroethylene homo- and copolymers, vinylidene fluoride homo- and copolymers, perfluoroalkoxy polymers and fluorinated ethylene-propylene copolymers.

32. A method in accordance with claim 31, wherein the fluoropolymer is an ethylene-tetrafluoroethylene copolymer.

33. A method in accordance with claim 29, wherein said energy absorbing compound is titanium dioxide.

34. A method in accordance with claim 29 or claim 33, wherein the organic compound is selected from the group consisting of sulfur-containing compounds, hydroxy-containing compounds, nitrogen-containing compounds, phosphorus containing compounds and carbonyl-containing compounds.

35. A method in accordance with claim 34, wherein the organic compound is selected from the group consisting of tetrakis (methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane, distearyl thiodipropionate, tris (2,4-di-t-butylphenyl)-4,4'-phosphite and triallyliscyanurate.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 90/00485

I. CLASSIFICATION OF SUBJECT MATTER (In several classification symbols specify indicate all) According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 08 K 13/02, C 08 L 27/12, B 41 M 1/30, 5/24, H 01 B 7/36, //(C 08 K 13/02, 3:22, 5:00)														
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched *</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border: 1px solid black;">Classification System</th> <th style="border: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: middle;">IPC⁵</td> <td style="border: 1px solid black; text-align: center; vertical-align: middle;">C 08 K, C 08 L, B 41 M, H 01 B</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *</div>			Classification System	Classification Symbols	IPC ⁵	C 08 K, C 08 L, B 41 M, H 01 B								
Classification System	Classification Symbols													
IPC ⁵	C 08 K, C 08 L, B 41 M, H 01 B													
III. DOCUMENTS CONSIDERED TO BE RELEVANT * <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; border: 1px solid black;">Category *</th> <th style="border: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 10%; border: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">P, A</td> <td style="border: 1px solid black; vertical-align: top;">EP, A, 0321091 (BICC PLC) 21 June 1989 see claims ---</td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 3557050 (SHUN KOIZUMI et al.) 19 January 1971 see claims; column 2, line 34 - column 3, line 27 ---</td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 3947525 (ARTHUR B. ROBERTSON et al.) 30 March 1976 see claims -----</td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	P, A	EP, A, 0321091 (BICC PLC) 21 June 1989 see claims ---	1	A	US, A, 3557050 (SHUN KOIZUMI et al.) 19 January 1971 see claims; column 2, line 34 - column 3, line 27 ---	1	A	US, A, 3947525 (ARTHUR B. ROBERTSON et al.) 30 March 1976 see claims -----	1
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁴</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 5th May 1990 </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center;">13 JUN 1990</div> </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority EUROPEAN PATENT OFFICE </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;">MISS LAZELAAR</div> </td> </tr> </table>			Date of the Actual Completion of the International Search 5th May 1990	Date of Mailing of this International Search Report <div style="text-align: center;">13 JUN 1990</div>	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer <div style="text-align: center;">MISS LAZELAAR</div>								
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9000485
SA 34125

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 06/06/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0321091	21-06-89	None	
US-A- 3557050	19-01-71	None	
US-A- 3947525	30-03-76	CA-A- 1025584	31-01-78
		JP-A, B, C49107350	11-10-74
		US-A- 4039631	02-08-77